(12) **EUROPEAN PATENT APPLICATION**

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(54) A process for preparation of silyl ketene acetals.

(57) What is disclosed is a process for the manufacture of
increased yields of high-purity silyl ketene acetals, the process
comprising a) contacting of methacrylic acid or an ester of
methacrylic acid with a hydrogen-containing silicon material in
the presence of a rhodium catalyst with inorganic ligands, and
b) separation and isolation of the desired product from the
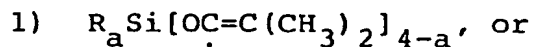crude product.

EP 0 219 322 A2

Description

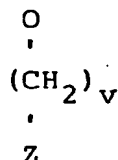# A PROCESS FOR PREPARATION OF SILYL KETENE ACETALS

This invention relates to improved yields from a process for preparing and purifying chemical intermediates ·
known as silyl ketene acetals. More specifically. the silyl ketene acetals are the reaction products of a vinylic
compound (methacrylic acid or one of its esters) and a hydrogen-containing silicon material.

To aid in the understanding of the instant invention. the following chemical definitions and notation will be
out-lined below. This notation will subsequently be used in the remainder of this specification: a. Silyl ketene
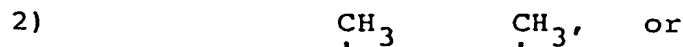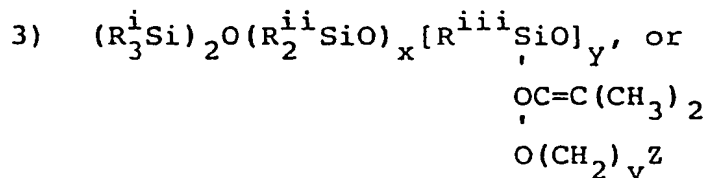acetal = SKA = 1,4- adduct =

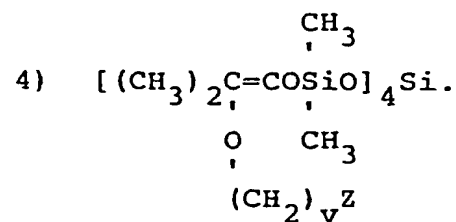1) $R_a Si[OC=C(CH_3)_2]_{4-a}$, or

$$\underset{\underset{Z}{\overset{|}{(CH_2)_v}}}{\overset{|}{\underset{|}{O}}}$$

2) $[(CH_3)_2 C=\underset{\underset{\underset{Z}{\overset{|}{(CH_2)_v}}}{\overset{|}{O}}}{\overset{|}{C}}-O-\underset{\underset{CH_3}{\overset{|}{CH_3}}}{\overset{CH_3}{\overset{|}{Si}}}-]_2 \; O \; [\underset{\underset{CH_3}{\overset{|}{CH_3}}}{\overset{CH_3'}{\overset{|}{Si}}}-O]_w$, or

3) $(R_3^i Si)_2 O(R_2^{ii} SiO)_x [R^{iii} \underset{\underset{O(CH_2)_v z}{\overset{|}{OC=C(CH_3)_2}}}{\overset{|}{Si}} O]_y$, or

4) $[(CH_3)_2 \underset{\underset{(CH_2)_v z}{\overset{|}{O}}}{\overset{\overset{CH_3}{\overset{|}{}}}{C=COSiO}]_4 Si$.

b. Vinylic compound = methacrylic acid or an ester of methyacrylic acid
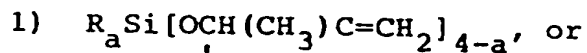
$$CH2=CH(CH_3)\overset{\overset{O}{\|}}{C}O(CH_2)_v Z$$
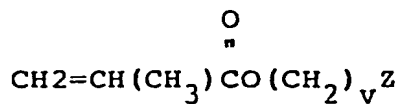
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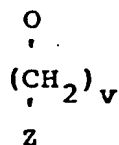
c. Major by-products

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*   Carbonyl adduct = CA = 1,2- adduct =

1) $R_a Si[OCH(CH_3)C=CH_2]_{4-a}$, or
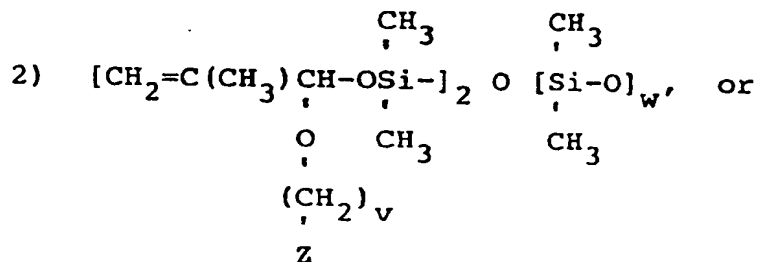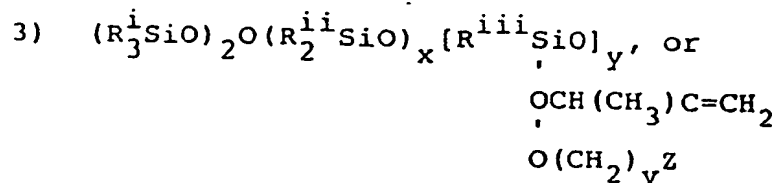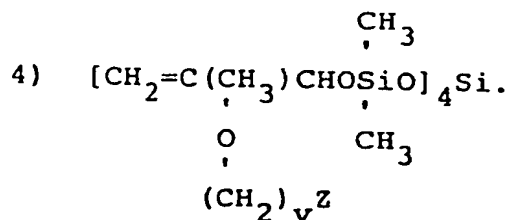
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$$O$$
$$(CH_2)_v$$
$$Z$$

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2) $[CH_2=C(CH_3)\overset{CH_3}{\underset{|}{CH-O}}\overset{CH_3}{\underset{|}{Si-}}]_2 O [\overset{CH_3}{\underset{CH_3}{Si-O}}]_w$, or

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$$O \quad CH_3$$
$$(CH_2)_v$$
$$Z$$

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3) $(R^i_3 SiO)_2 O(R^{ii}_2 SiO)_x [R^{iii}SiO]_y$, or

$$OCH(CH_3)C=CH_2$$
$$O(CH_2)_v Z$$

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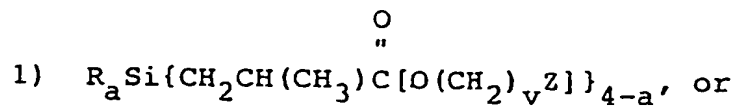4) $[CH_2=C(CH_3)\overset{CH_3}{\underset{|}{CHOSiO}}]_4 Si.$

$$O \quad CH_3$$
$$(CH_2)_v Z$$

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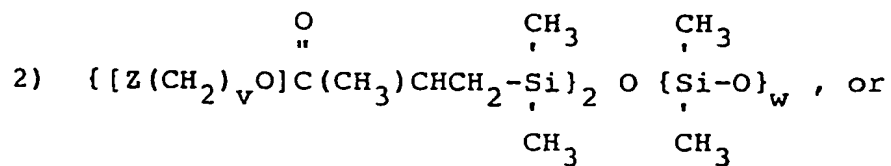
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* Beta- or vinyl adduct = VA =

1) $R_aSi\{CH_2CH(CH_3)\overset{O}{\overset{\|}{C}}[O(CH_2)_vZ]\}_{4-a}$, or

2) $\{[Z(CH_2)_vO]\overset{O}{\overset{\|}{C}}(CH_3)CHCH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\}_2 O \underset{\underset{CH_3}{|}}{\{\overset{\overset{CH_3}{|}}{Si}-O\}}_w$, or

3) $(R_3^iSi)_2O(R_2^{ii}SiO)_x\{\underset{\underset{CH_2CH(CH_3)\overset{O}{\overset{\|}{C}}[OCH_2)_vZ]}{|}}{R^{iii}Si}\}_y$, or

4) $[Z(CH_2)_v O\overset{O}{\overset{\|}{C}}(CH_3)CHCH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}O]_4Si.$

d. Hydrogen-containing silicon material =

1) R_aSiH_{4-a}, or

2) $(H\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-)_2 O (\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}})_w$

3) $(R_3^i Si)_2 O(R_2^{ii} SiO)_x (R^{iii} HSiO)_y$,

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$$4) \quad [HSiO]_4 Si.$$
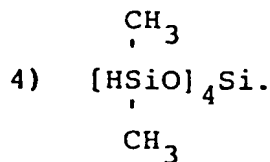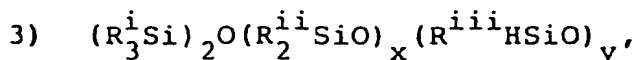with CH_3 above and below the $HSiO$ bracket marked by dots.

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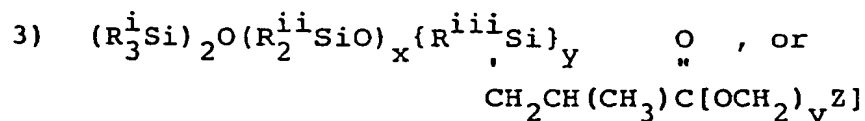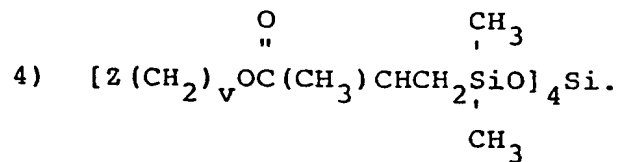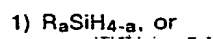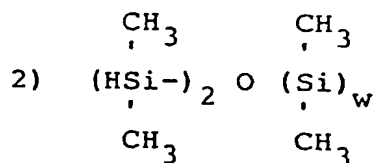
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Further details on the chemical structures and notation will be given later in the specification.

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The first reference to preparation of silyl ketene acetals was in the late-1950's by Petrov et al., (J. Gen. Chem. (USSR), 29(1959), pp. 2896-2899). This reference and most of the other references to the art deal with the chemical species of the general formula,

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$$R_3 Si [OC=(CH_3)_2].$$
$$O(CH_2)_v Z$$

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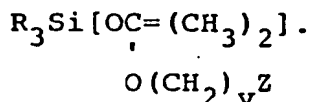
These reactive organosilane intermediates are of interest because of the ability to further react the SKA's to other intermediates which would be difficult to synthesize by other means. A very recent application is the use of the SKA materials as acrylate polymerization initiators. This concept known as Group Transfer Polymerization (GTP) was developed by DuPont and is disclosed in three recent U.S. patents, U.S. 4,414,372, Farnham et al., issued November 8, 1983; U.S. 4,417,034, Webster, issued November 22, 1983; and U.S. 4,508,880, Webster, issued April 2, 1985.

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Silyl ketene acetals, with two silyl ketene acetal moieties. having the general formula,

$$R_2 Si [OC=C(CH_3)_2]_2$$
$$O(CH_2)_v Z$$

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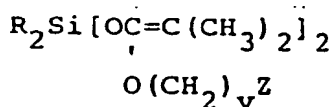
are also disclosed in the art. Kita et al. (Tetrahedron Letters. 24:12 (1983). pp. 1273-1276). disclose the preparation of several ketene acetal materials. Among these SKA materials are the bifunctional compounds,
{(CH3)2C = C[O(CH3)]O}2Si(CH3)(CH3),
{(CH3)2C = C[O(CH3)]O}2Si(C2H5)(C2H5),
{(CH3)2C = C[O(CH3)]O}2Si(i-C3H7)(i-C3H7), and
{(CH3)2C = C[O(CH3)]O}2Si(CH3)(C6H5).

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These novel SKA reagents have been shown to be very useful as bifunctional protecting agents for H-acidic materials such as diols, dithiols, diacids, and the like.

Three procedures for preparing silyl ketene acetals from carboxylic acid esters are known in the art. The first general route to SKA's is the reaction of a carboxylic acid ester with an appropriate metal reagent to form a metal enolate ion and subsequent reaction of the enolate ion with an organochlorosilane. Ainsworth et al.. J. Organometallic Chem., 46(1972). pp. 59-71 described the preparation of an SKA via the reaction of carboxylic acid esters with lithium diisopropylamide, followed by reaction with trimethylchlorosilane. Kita et al., in the above cited reference, disclose a similar procedure to prepare the bifunctional SKA's. Brown J.Org. Chem.. 39:9(1974). pp. 1324-1325, describes the preparation of metal enolate ions by reacting potassium hydride in tetrahydrofuran with a carbonyl compound, followed by reaction with excess triethylamine and trimethylchlorosilane.

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In a second general procedure silyl ketene acetals are prepared by the hydrosilation reaction of carboxylic acid esters and organohydrosilanes. Petrov et al., J. Gen. Chem. (USSR), 29(1959), pp. 2896-2899, described the platinum-catalyzed reaction of methylmethacrylate with triethylsilane; the product was mainly the beta or

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vinyl adduct VA rather than the desired SKA. Ojima et al., J. Organometallic Chem., 111(1976), pp. 43-60, studied the use of tris(triphenylphosphine)rhodium chloride as a catalyst; methacrylate esters and triethylsilane formed mainly the desired SKA with some carbonyl adduct CA. Ojima et al. include an example in which a crude reaction product is determined to be 92% SKA and 8% CA by gas chromatographic analysis. Ojima et al. make no disclosure of separation and recovery of SKA essentially free of CA.

Howe et al., J. Organometallic Chem., 208(1981), pp. 401-406 and Yoshii et al., Chem. Pharm. Bull., 22(1974), pp. 2767-2769, describe yields of 70-75% SKA from the reaction of $(C_2H_5)_3SiH$ and methylmethacrylate using organophosphorous complexes of rhodium as a catalyst. Howe determined yield by use of gas chromatographic analyses. Nowhere does Howe et al. mention the carbonyl adduct or physical separation and isolation of the desired SKA material. Yoshii et al. indicate that the SKA produced above was recovered by "short-path distillation." In the instant invention, it was unexpectedly found that for methacrylate materials the carbonyl adduct CA was formed along with the desired SKA and that separation of the SKA from CA was not possible by conventional distillation. The very close boiling points of the SKA and CA (estimated as a difference of less than 5°C. by gas chromatographic and mass spectroscopic work) would seem to bear out this finding. Further, during the development of the instant invention, it was unexpectedly found that the use of gas chromatography to analyze for the SKA and CA components in the crude reaction mixture was in itself difficult. The early attempts at gas chromatography resulted in identification of SKA and CA as a single compound. A special gas chromatographic technique was required to effect resolution of the SKA and CA peaks to facilitate identification. This analytical difficulty may further explain the apparent contradiction between the teachings of Yoshii et al. and the instant invention. Yoshii et al. may have recovered SKA and CA together and may have identified this mixture as SKA.

In a third procedure, Ishikawa et al. in U.S. 4,482,729, issued November 13, 1984, describe the preparation of a fluoroalkyl silyl ketene acetal by the reaction of a fluorinated carboxylic acid ester with trimethylsilyl trifluoromethanesulfonate.

Preparation of silyl ketene acetals via the metal enolate ion route has several shortcomings compared to the instant invention. First there is the cost of the necessary reactants, namely, lithium diisopropylamide, potassium hydride, solvents, etc. Additionally, the resultant metal salts formed during the reaction pose a difficult processing step. In combination, the two above shortcomings result in potentially higher costs to produce the final product.

In regard to the art on use of rhodium catalysts, the references cited teach the use of organophosphorous complexes of rhodium. The instant invention has found unexpectedly that $RhCl_3.3H_2O$, an inexpensive, more readily available material, is an improved catalyst compared to the cited organophosphorous complexes of rhodium. Significantly, it has been found that $RhCl_3.3H_2O$ will give the desired results, that is, reactivity and selectivity with some methacrylate esters, where the organophosphorous complexes will not. Most significantly, it has also been unexpectedly found that $RhCl_3.3H_2O$ increases yields of the desired silyl ketene acetal in the crude reaction mixture by as much as 50 percent or more, as compared to comparable levels of organorhodium complexes.

A further unexpected result of the instant invention was the finding that rhodium catalyst concentration has a significant impact upon the selectivity toward the desired silyl ketene acetal. An additional unexpected result is the finding that the carbonyl adduct (CA), which boiled very closely to the desired SKA, could be reacted to higher-boiling chemical species by reaction with an excess of the hydrogen-containing silicon material. This finding allowed the use of conventional separation techniques such as distillation to facilitate what is an extremely difficult separation and enhances the recovery of very high-purity SKA.
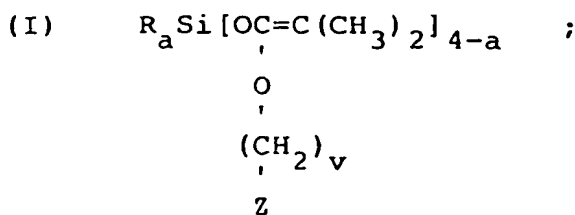
One example of the utility of reacting the carbonyl adduct (CA) to higher-boiling chemical species to facilitate recovery of high-purity silyl ketene acetal SKA via distillation is included in the examples. A further example of the utility of this finding in facilitating the separation and isolation of desired SKA materials is included in another U.S. patent application filed concurrently with the instant application. The application in reference, which was filed on behalf of William X. Bajzer and Anthony Revis and is entitled PREPARATION OF HIGH-PURITY SILYL KETENE ACETALS, was filed on even date herewith.

The objective of the instant invention is to provide a process for the preparation and recovery of silyl ketene acetals; said process 1) provides for higher yields of the desired SKA in the crude reaction product , 2) maximizes conversion of raw materials to the desired SKA, 3) provides a purification and recovery scheme to yield high-purity final SKA product, 4) minimizes complexity of processing, and 5) minimizes the final cost of the desired SKA product.

In accordance with the instant invention, there is provided a process for the manufacture of increased yields of high-purity silyl ketene acetal material of the general formula selected from the group consisting essentially of
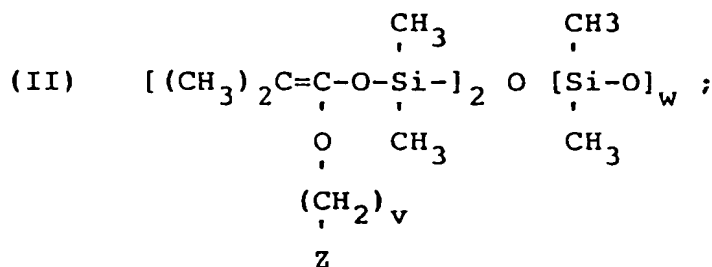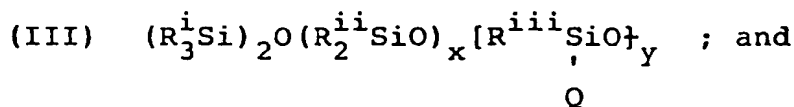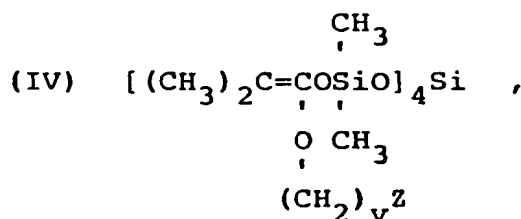
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(I) $R_a Si[O\underset{\underset{O}{|}}{C}=C(CH_3)_2]_{4-a}$;

$\underset{\underset{Z}{|}}{(CH_2)_v}$

(II) $[(CH_3)_2C=\underset{\underset{O}{|}}{C}-O-\underset{\underset{CH_3}{|}}{\underset{|}{Si}}-]_2 O [\underset{\underset{CH_3}{|}}{\underset{|}{Si}}-O]_w$;

$\underset{\underset{Z}{|}}{(CH_2)_v}$

(III) $(R^i_3Si)_2 O(R^{ii}_2SiO)_x[R^{iii}\underset{\underset{Q}{|}}{Si}O]_y$; and

(IV) $[(CH_3)_2C=\underset{\underset{O}{|}}{C}O\underset{\underset{CH_3}{|}}{Si}O]_4 Si$,

$(CH_2)_v Z$

wherein R is selected from the group consisting of alkyl radicals containing 1 to 4 carbon atoms, aryl groups, and alkoxy groups containing 1 to 4 carbon atoms;
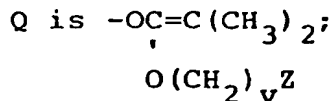$\underline{a}$ has a value of 0, 1, 2, or 3;
$\underline{v}$ in each case has a value of 0, 1, 2 or 3;
$\underline{w}$ has a value of 0 to 25;
$\underline{x}$ has a value of 0 to 100;
$\underline{y}$ has a value of 1 to 35;

Q is $-O\underset{\underset{O(CH_2)_v Z}{|}}{C}=C(CH_3)_2$;

R^i, R^{ii}, and R^{iii} are each independently selected from the group consisting of alkyl groups containing 1 to 4 carbon atoms and aryl groups; Z in each case is independently selected from the group consisting of   (i) -H,
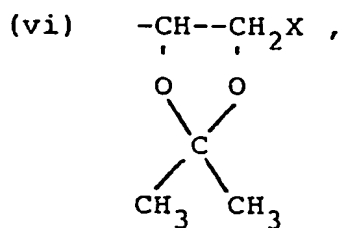   (ii) -OH,
   (iii) -SiR^{iv}R^{v}R^{vi},
   wherein R^{iv}, R^v, and R^{vi} are independently selected from the group consisting of alkyl radicals containing 1 to 4 carbon atoms, aryl groups, and alkoxy groups containing 1 to 4 carbon atoms.
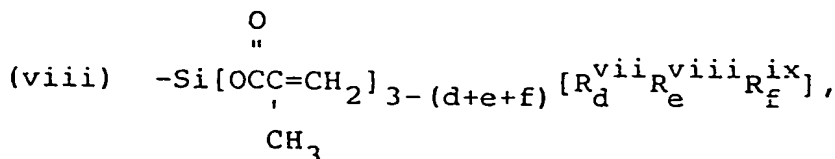   (iv) -OSiR^{iv}R^{v}R^{vi},
   (v) -CH(CH3)2.

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(vi)
$$-CH-CH_2X \ ,$$

with the CH bearing two oxygens forming a ring to a central C bearing two CH_3 groups:

$$
\begin{array}{c}
-CH-CH_2X \\
\ \ O \quad O \\
\ \ \diagdown \diagup \\
\ \ \ C \\
\ \diagup \ \diagdown \\
CH_3 \quad CH_3
\end{array}
$$

wherein X is hydrogen or $-(CH_2)_{0-5}(CH_3)$.

(vii) $-(CH_2)_bOCH(CH_3)O(CH_2)_cCH_3$,

wherein b and c each have a value of 1 to 4.

(viii)
$$-Si[OC\overset{\overset{\textstyle O}{\|}}{C}=CH_2]_{3-(d+e+f)} [R_d^{vii}R_e^{viii}R_f^{ix}] \ ,$$
with a CH_3 on the central carbon:
$$-Si[O\overset{\overset{\textstyle O}{\|}}{C}\underset{\underset{\textstyle CH_3}{|}}{C}=CH_2]_{3-(d+e+f)} [R_d^{vii}R_e^{viii}R_f^{ix}] \ ,$$

wherein R^{vii}, R^{viii}, and R^{ix} are independently selected from and have the same definition as R^{iv}, R^v, and R^{vi}; and wherein d, e, and f each have a value of 0 or 1.

(ix) $-NR^xR^{xi}$,

wherein R^x and R^{xi} are independently selected from and have the same definition as R^{iv}, R^v, and R^{vi},

(x) $-Y$,

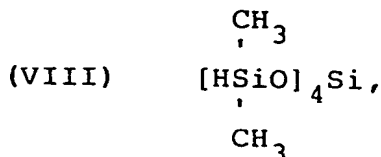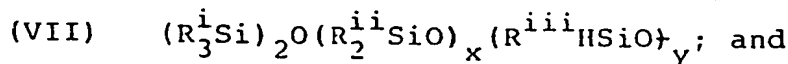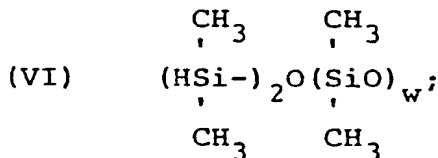wherein Y is independently selected from a group consisting of C_{1-20} alkyl, alkenyl, or alkadienyl; C_{6-20} cycloalkyl, aryl, alkaryl, or aralkyl; any of said groups containing one or more ether oxygen atoms within aliphatic segments thereof; and any of such groups containing one or more functional substituents that are unreactive under polymerizing conditions.

(xi) $-N=C=O$,

the process comprising the reaction of a vinylic compound with a hydrogen-containing silicon material under certain conditions as will be delineated herein. What is described, therefore, is a process to facilitate recovery of a high-purity silyl ketene acetal, said process comprising (A) contacting (I), a vinylic compound selected from the group consisting of [i] methacrylic acid and [ii] an ester of methacrylic acid of the general chemical formula,

$$CH_2 = C(CH_3)\overset{\overset{\textstyle O}{\|}}{C}O(CH_2)_vZ,$$
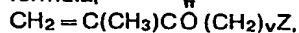
wherein, v and Z are defined above, with a hydrogen-containing silicon material having the general formulae,

(V) R_aSiH_{4-a};

(VI)
$$(H\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{Si}}-)_2O(\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{Si}}O)_w;$$

(VII)
$$(R_3^iSi)_2O(R_2^{ii}SiO)_x(R^{iii}HSiO)_y; \quad and$$

(VIII)
$$[H\underset{\underset{\textstyle CH_3}{|}}{SiO}]_4Si,$$

wherein, R^i, R^{ii}, R^{iii}, a, w, x, and y have the meanings defined above, in the presence of a rhodium compound containing only inorganic ligands; (B) separating and isolating the desired product from the reaction mixture.

As described above, the catalyst is a rhodium compound containing only inorganic ligands such as $RhCl_3.3H_2O$ or the like. In whatever form the catalyst is utilized, the rhodium concentration relative to the vinylic compound should be at least 50 ppm on a molar basis. As will be described in the examples, the concentration of the rhodium catalyst is a critical factor in maximizing rate of reaction and silyl ketene acetal content of the resultant crude product.

The temperature during reaction of the hydrogen-containing silicon material and the vinylic compound is maintained in a range of 30° to 80°C. The lower temperature is a minimum to ensure that sufficient rate of reaction is achieved. The upper temperature is specified to minimize the polymerization of the vinylic compound.

The pressure in the reaction zone during the reaction of the hydrogen-containing silicon material and the vinylic compound is at least atmospheric pressure. As will be shown in the examples, pressures up to and including 200 psig do not have a negative effect upon the reaction of the instant invention.
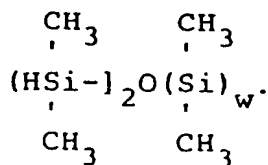
The hydrogen-containing silicon material and the vinylic compound are contacted in the presence of the rhodium catalyst at reaction conditions for a period of time of at least one hour.

Additionally, a molar excess of the hydrogen-containing silicon material of at least 12% relative to the vinylic compound is needed to ensure conversion of the very close-boiling carbonyl adduct.

As will be noted in the examples, conversion of the carbonyl adduct to higher-boiling materials with an excess of the hydrogen-containing silicon material facilitates recovery of product that is greater than 95 weight percent silyl ketene acetal, with less than 1 weight percent of the carbonyl adduct as an impurity. Conventional distillation column design can be specified to provide the capabilities to recover silyl ketene acetal at greater than 95 weight percent purity.
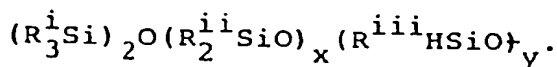
The hydrogen-containing silicon material may be of the general formula, R_aSiH_{4-a}. Hydrogen-containing silicon materials having this general formula include, for example, $(CH_3)_3SiH$, $(CH_3)_2SiH_2$, CH_3SiH_3, SiH_4, and the like.

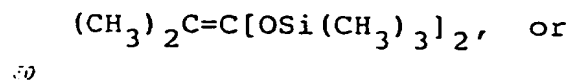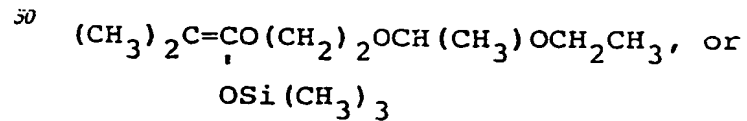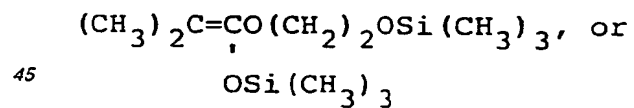The hydrogen-containing silicon material may also have the general formula,

$$(HSi-]_2O(Si)_w . \begin{array}{cc} CH_3 & CH_3 \\ | & | \\ | & | \\ CH_3 & CH_3 \end{array}$$
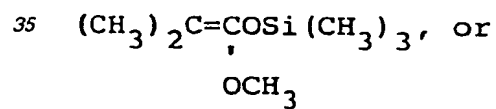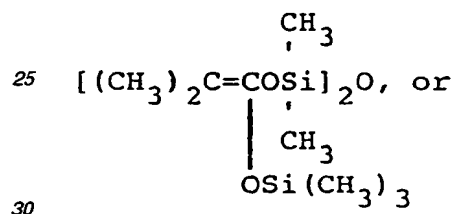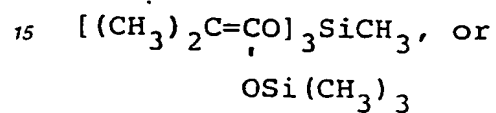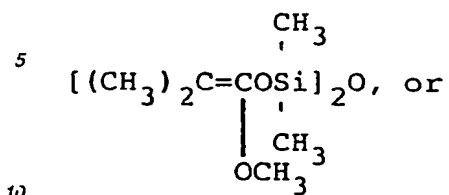
Hydrogen-containing silicon compounds having this general formula include, for example $[(CH_3)_2HSi]_2O$, $[(CH_3)_2HSiO]_2[(CH_3)_2SiO]_{1-25}$, and the like.

The hydrogen-containing silicon material may further have the general formula,

$$(R_3^iSi)_2O(R_2^{ii}SiO)_x(R^{iii}HSiO)_y .$$

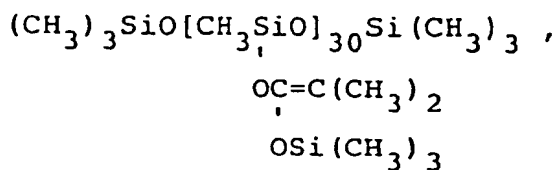Hydrogen-containing silicon compounds having this general formula include, for example, $(CH_3)_3SiO[CH_3H-SiO]Si(CH_3)_3$, $[(CH_3)_3SiO][CH_3)_2SiO][CH_3HSiO][Si(CH_3)_3]$, $[(CH_3)_3SiO][CH_3HSiO]_{2-35}[Si(CH_3)_3]$, $[(CH_3)_3SiO][(CH_3)_2SiO]_{2-100}[CH_3HSiO]_{2-35}[Si(CH_3)_3]$, and the like.
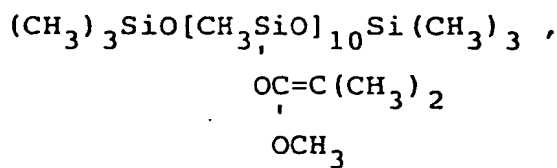
The silyl ketene acetal may have the formula,

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$$[(CH_3)_2C=\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OCH_3}{|}}{\underset{\displaystyle CH_3}{Si}}}]_2O, \text{ or}$$

$$[(CH_3)_2C=\overset{|}{\underset{|}{CO}}]_3SiCH_3, \text{ or}$$
$$OSi(CH_3)_3$$

$$[(CH_3)_2C=\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OSi(CH_3)_3}{|}}{\underset{\displaystyle CH_3}{Si}}}]_2O, \text{ or}$$

$$(CH_3)_2C=\overset{|}{\underset{|}{CO}}Si(CH_3)_3, \text{ or}$$
$$OCH_3$$

$$(CH_3)_2C=\overset{|}{\underset{|}{CO}}(CH_2)_2OSi(CH_3)_3, \text{ or}$$
$$OSi(CH_3)_3$$

$$(CH_3)_2C=\overset{|}{\underset{|}{CO}}(CH_2)_2OCH(CH_3)OCH_2CH_3, \text{ or}$$
$$OSi(CH_3)_3$$

$$(CH_3)_2C=C[OSi(CH_3)_3]_2, \text{ or}$$

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$(CH_3)_3SiO[CH_3SiO]_{30}Si(CH_3)_3,$
$$OC=C(CH_3)_2$$
$$OCH_3$$

$(CH_3)_3SiO[CH_3SiO]_{30}Si(CH_3)_3,$
$$OC=C(CH_3)_2$$
$$OSi(CH_3)_3$$

$(CH_3)_3SiO[CH_3SiO]_{10}Si(CH_3)_3,$
$$OC=C(CH_3)_2$$
$$OCH_3$$

$(CH_3)_3SiO[CH_3SiO]_{10}Si(CH_3)_3,$
$$OC=C(CH_3)_2$$
$$OSi(CH_3)_3$$

$(CH_3)_3SiO[CH_3SiO]_3Si(CH_3)_3,$
$$OC=C(CH_3)_2$$
$$OCH_3$$

$(CH_3)_3SiO[CH_3SiO]_3Si(CH_3)_3,$ or the like.
$$OC=C(CH_3)_2$$
$$OSi(CH_3)_3$$
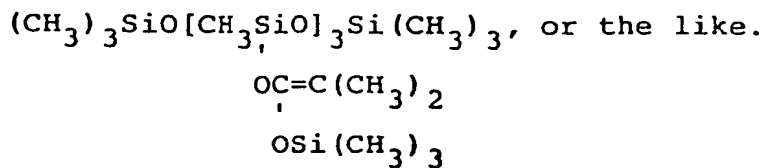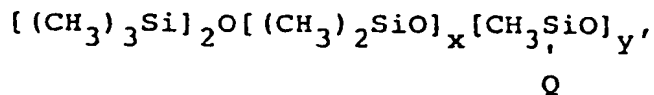
The silyl ketene acetal may further have the general formula.

$[(CH_3)_3Si]_2O[(CH_3)_2SiO]_x[CH_3SiO]_y,$
$$Q$$

wherein Q is defined as being

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$$-O\overset{\cdot}{C}=C(CH_3)_2 \qquad \text{or}$$
$$OCH_3$$

$$-O\overset{\cdot}{C}=C(CH_3)_2 \cdot$$
$$OSi(CH_3)_3$$
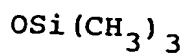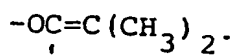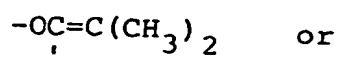
Silyl ketene acetals having this general formula can be

$$(CH_3)_3SiO[CH_3\overset{\cdot}{S}iO]Si(CH_3)_3, \text{ or}$$
$$O\overset{\cdot}{C}=C(CH_3)_2$$
$$OCH_3$$

$$(CH_3)_3SiO[CH_3\overset{\cdot}{S}iO]Si(CH_3)_3, \text{ or}$$
$$O\overset{\cdot}{C}=C(CH_3)_2$$
$$OSi(CH_3)_3$$

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$$(CH_3)_3SiO[(CH_3)_2SiO][CH_3SiO]Si(CH_3)_3, \text{ or}$$
$$OC=C(CH_3)_2$$
$$OCH_3$$

$$(CH_3)_3SiO[(CH_3)_2SiO][CH_3SiO]Si(CH_3)_3, \text{ or}$$
$$OC=C(CH_3)_2$$
$$OSi(CH_3)_3$$

$$(CH_3)_3SiO[(CH_3)_2SiO]_{2-100}[CH_3SiO]_{2-35}Si(CH_3)_3, \text{ or}$$
$$OC=C(CH_3)_2$$
$$OCH_3$$

$$(CH_3)_3SiO[(CH_3)_2SiO]_{2-100}[CH_3SiO]_{2-35}Si(CH_3)_3, \text{ or}$$
$$OC=C(CH_3)_2$$
$$OSi(CH_3)_3$$

$$(CH_3)_3SiO[CH_3SiO]_{2-35}Si(CH_3)_3, \text{ or}$$
$$OC=C(CH_3)_2$$
$$OCH_3$$

$$(CH_3)_3SiO[CH_3SiO]_{2-35}Si(CH_3)_3, \text{ and the like.}$$
$$OC=C(CH_3)_2$$
$$OSi(CH_3)_3$$
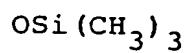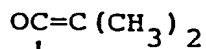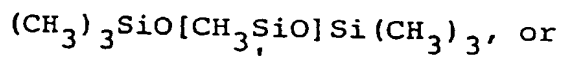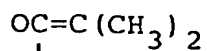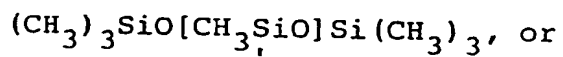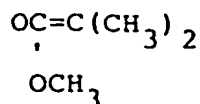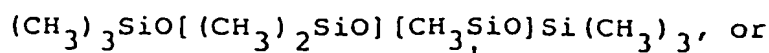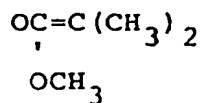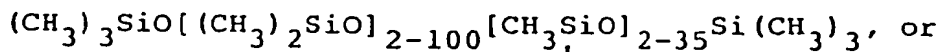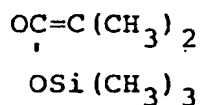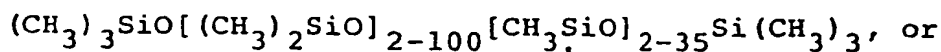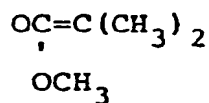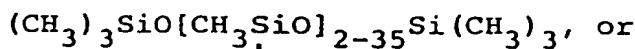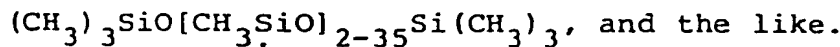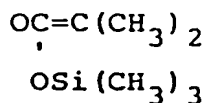
The preferred mode for carrying out the instant invention is to add the hydrogen-containing silicon material to a mixture of the vinylic compound and a solvent solution of $RhCl_3.3H_2O$. The rhodium concentra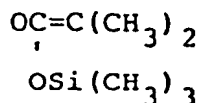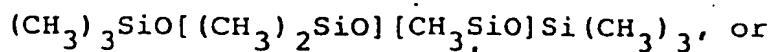tion should be between 50 and 3000 ppm on a molar basis relative to the vinylic compound. More preferably, the rhodium concentration should be between 200 and 3000 ppm.

The hydrogen-containing silicon material should be added at such a rate that the reaction temperature is maintained preferably between 40° and 60°C.

The reaction is preferably operated at atmospheric pressure.

Excess of the hydrogen-containing silicon material fed to the reaction mixture is preferably 12 to 25 mole percent relative to the vinylic compound.

Distillation conditions are maintained so that processing temperatures are kept as low as possible to minimize degradation of the desired SKA. Specification of the distillation column (theoretical trays, etc..) is known in the art and should be set to maintain a silyl ketene acetal purity of greater than 95 weight percent, with less than 1 weight percent byproduct CA as an impurity.

So that those skilled in the art can better appreciate and understand the instant invention, the following examples are given. These examples are presented to be illustrative and are not to be construed as limiting the instant invention as delineated in the claims.

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Example 1

Two series of runs were made to compare the effectiveness of an organo complex of rhodium with a rhodium compound with inorganic ligands. as a catalyst for the reaction of methylmethacrylate (MMA) and $(CH_3)_3SiH$ to produce the desired silyl ketene acetal (SKA) or 1,4-adduct.

$(CH_3)_2C=C(OCH_3)$ $[OSi(CH_3)_3]$.

The following general procedures were used for all the runs utilizing an organo complex of rhodium as a catalyst:

2527 grams (25.2 moles) of MMA. 4.67 grams (0.005 moles) tris(triphenylphosphine)rhodium chloride, and 0.25 gram of methoxyhydroquinone were charged to a 2-gallon pressure reactor with agitator. The rhodium catalyst charge was varied to vary the catalyst concentration. The reactor was pressurized with nitrogen gas which contained 2 volume percent oxygen. Reactor pressure was maintained with this gas mixture. The reactor was pressurized to 80 to 200 psig. Temperature was controlled by a cooling/heating coil in the reactor. Reactor temperature was further controlled by the addition rate of $(CH_3)_3SiH$.

$(CH_3)_3SiH$ was fed as a liquid to the reactor via a proportioning pump through a dip pipe. A total of 3513 milliliters (2241 grams or 30.3 moles) of $(CH_3)_3SiH$ were fed to the reactor over a period of approximately 2 to 3 hours. Post-heating at temperature after $(CH_3)_3SiH$ addition was approximately 4 to 5 hours. Reaction temperature was controlled by the rate of addition of $(CH_3)_3SiH$ and cooling of the reactor.

The results of gas chromatographic analyses of crude product samples for this series of runs are tabulated below. These crude product samples are designated as Samples A. B, C, D, E, and F, respectively. Catalyst concentration (Rh) is expressed as ppm in MMA on a molar basis. Temperature is expressed in °C. Crude product analysis is expressed as weight percent MMA. SKA, and the carbonyl or 1,2-adduct (CA), the vinyl adduct (VA). and other by-products, where

$CH_2=C(CH_3)CH(OCH_3)$ $[OSi(CH_3)_3]$ = CA

$(CH_3)_3SiCH_2C(CH_3)COOCH_3$ = VA.
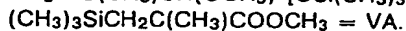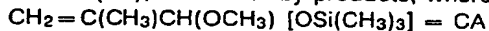
Results are tabulated as Table 1:

Table 1

(Not Within Scope of the Instant Invention)

Sample	Rh	Temp	MMA	SKA	CA	VA	Other
A	200	40	2.2	54.1	6.8	7.6	29.3
B	200	50	4.2	47.8	6.0	11.5	30.5
C	200	55	0	41.3	2.3	11.5	44.9
D	400	40	0.5	74.3	4.8	1.6	18.8
E	400	45	5.3	80.5	10.4	0.4	3.4
F	400	55	2.3	63.5	6.2	1.3	29.0

A second series of runs was made using $RhCl_3.3H_2O$ as the catalyst for the reaction of methylmethacrylate (MMA) with $(CH_3)_3SiH$ to produce the desired SKA as above. $RhCl_3.3H_2O$ is not soluble in MMA. Therefore, the $RhCl_3.3H_2O$ was dissolved in acetone (1 part $RhCl_3.3H_2O$ per 40 parts acetone). The $RhCl_3.3H_2O$ was introduced to the reactor as a solution. All runs in this series followed the general procedure given below: 200 grams (2 moles) of MMA and 0.2 grams of methoxyhydroquinone were charged to an agitated reactor with heating and cooling capabilities. $RhCl_3.3H_2O$ was added to the reactor as an acetone solution (1 part $RhCl_3.3H_2O$ per 40 parts of acetone). 2.4 grams of this solution or 0.06 grams (2.2×10^{-4} moles of $RhCl_3.3H_2O$) were charged to the reactor. The reactor and contents were heated to the desired reaction temperature (45-75°C.). The reactor also had cooling capability. During the course of the reaction. the system was at essentially atmospheric pressure. Additionally. the reactor was continuously purged with nitrogen gas which contained 2 volume percent oxygen.

$(CH_3)_3SiH$ was stored as a liquid and fed to the reactor as a gas. 149 grams (2 moles) of $(CH_3)_3SiH$ were fed to the reactor over a period of 2 to 4 hours to maintain the reaction temperature. Crude product samples were taken and analyzed via gas chromatography. These samples are designated Sample G, H, I, J, K, L. M, N, and O. respectively.

Results are again tabulated below to show the effect of rhodium catalyst concentration and reaction temperature upon crude product composition. These results are summarized. with the same notation as described above, as Table 2:

Table 2

Sample	Rh	Temp	MMA	SKA	CA	VA	Other
G	50	55	43.8	44.6	5.2	0.7	6.3
H	50	65	44.7	46.4	5.6	0.4	2.9
I	50	75	33.9	52.4	6.8	0.2	6.7
J	100	50	32.0	56.0	6.9	0.1	5.0
K	100	60	12.3	68.2	6.9	1.2	11.4
L	100	70	24.8	62.8	7.1	1.3	4.0
M	200	45	0.4	86.0	9.8	0.8	3.0
N	200	55	0.4	84.1	9.9	0	5.6
O	200	65	5.2	81.1	11.2	0.4	2.1

These results demonstrate that $RhCl_3.3H_2O$ is a more efficient catalyst than tris(triphenylphosphine)rhodium in preparing the desired SKA. Comparison of results illustrates the following advantages of $RhCl_3.3H_2O$ over tris(triphenylphosphine)rhodium chloride: 1) increased levels of SKA of 50% or more in crude reaction product at comparable rhodium catalyst levels; 2) lower levels of VA and other byproducts at comparable SKA levels, particularly at lower rhodium catalyst levels.

The above results also demonstrate that the reaction of MMA and $(CH_3)_3SiH$ to produce the desired silyl ketene acetal is improved by higher levels of $RhCl_3.3H_2O$.

These results also demonstrate that the reaction proceeds at atmospheric pressure.

Example 2

A run was made to study the progress of the rhodium-catalyzed reaction of $(CH_3)_3SiH$ and methylmethacrylate (MMA) to produce the desired silyl ketene acetal. Crude product composition was tracked as a function of $(CH_3)_3SiH$ addition.

200 grams (2 moles) of MMA were charged to an agitated reactor. $RhCl_3.3H_2O$ was added to the reactor as an acetone solution (1 part $RhCl_3.3H_2O$ per 40 parts of acetone). 2.4 grams of solution or 0.06 grams (2.2×10^{-4} moles) $RhCl_3.3H_2O$ were also added to the reactor. The run was made essentially at atmospheric pressure. The reactor was continuously purged with nitrogen gas which contained 2 volume percent oxygen. The reactor had both heating and cooling capabilities. The reactor was heated to 55°C., and that temperature was maintained throughout the course of the reaction.

$(CH_3)_3SiH$ was stored as a liquid and fed to the reactor as a gas. A total of 169 grams (2.28 moles) of $(CH_3)_3SiH$ was fed to the reactor. Samples of reaction crude were taken during the course of the $(CH_3)_3SiH$ addition. These samples are designated as Samples A, B, C, D, E, F, and G, respectively.

Table 3 is a summary of this sampling and subsequent analyses. Each sample is identified by the time after start of $(CH_3)_3SiH$ addition, mole percent (% $(CH_3)_3Si$) of the stoichiometric $(CH_3)_3SiH$ fed, and the crude product analysis.

Product analyses were effected by gas chromatography. The analyses are reported as weight percent (%) unreacted MMA and the silyl ketene acetal product and its major byproduct (abbreviated notation as described in Example 1).

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Table 3

Sample	Time,hr	% $(CH_3)_3SiH$	MMA	SKA	CA
A	1.0	26	60.7	35.7	6.7
B	2.0	54	31.2	58.4	7.6
C	3.0	78	13.7	77.5	10.3
D	4.1	101	0.1	84.1	9.9
E	4.7	106	0	86.4	6.1
F	5.2	110	0	80.4	2.6
G	5.8	114	0	82.7	1.3

The above results demonstrate the reduction of CA in the crude product by addition of excess $(CH_3)_3SiH$. The results would indicate that an excess of at least 12 mole percent of $(CH_3)_3SiH$, relative to MMA, is needed to react with the carbonyl adduct (CA) to facilitate later recovery of the desired silyl ketene acetal.

Example 3

A second run was made similarly to the run in Example 2 in which the $RhCl_3.3H_2O$ catalyzed reaction of $(CH_3)_3SiH$ and methylmethacrylate (MMA) was tracked as a function of $(CH_3)_3SiH$ addition. However, this particular run was carried out at a pressure of 100 psig. These results will be compared to those of Example 2.

75 grams (0.75 moles) of MMA were charged to an agitated reactor. 0.044 grams (1.7×10^{-4} moles) $RhCl_3.3H_2O$ dissolved in 1.3 grams acetone were also added to the reactor. The reactor was pressurized to 100 psig with a mixture of 2 mole percent oxygen in nitrogen gas. The reactor was heated to 55°C., and that temperature was maintained throughout the course of the reaction.

$(CH_3)_3SiH$ was added to the reactor as a liquid. A total of 66 grams (0.89 moles) of $(CH_3)_3SiH$ was fed to the reactor. Samples of reaction crude were taken during the course of the $(CH_3)_3SiH$ addition. These samples are designated Sample H, I, and J, respectively.

Table 4 is a summary of this sampling and subsequent analyses by gas chromatography. Each sample is identified by the time after start of the $(CH_3)_3SiH$ addition, mole percent [% $(CH_3)_3SiH$] of stoichiometric $(CH_3)_3SiH$ fed, and the subsequent crude product analysis. The analyses are reported using the notation of Example 2.

Table 4

Sample	Time,hr	% $(CH_3)_3SiH$	MMA	SKA	CA
H	4.5	100	0.3	79.7	9.9
I	5.5	106	0	76.6	6.0
J	6.5	117	0	75.2	0.1

Comparable results from Example 2 are shown in Table 5.

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Table 5

Sample	Time,hr	%(CH$_3$)$_3$SiH	MMA	SKA	CA
D	4.1	101	0.1	84.1	9.9
E	4.7	106	0	86.4	6.1
G	5.8	114	0	82.7	1.3

The above results demonstrate that pressure has little effect upon the course of the reaction to form the desired SKA and subsequent reaction of CA to higher-boiling byproducts.

Example 4

Two runs were made to produce a crude silyl ketene acetal from the reaction of (CH₃)₃SiH and 4-methyl-3,5-dioxy heptylmethacrylate,
CH₂ = C(CH₃)COOCH₂CH₂OCH(CH₃)OCH₂CH₃.

In the first run, 1 gram (0.005 moles) of 4-methyl-3,5-dioxyheptyl methacrylate, greater than 1 gram (greater than 0.005 moles) of (CH₃)₃SiH, and approximately 0.005 grams (5x10⁻⁶ moles) of tris(triphenylphosphine)rhodium chloride are charged to a sealed, agitated reactor. The reaction was allowed to proceed at ambient temperature. Samples were taken periodically and analyzed by gas chromatography. these samples were designated Samples A, B, C, and D, respectively.

Table 6 is a summary of the above analyses as a function of reaction time. Analysis of SKA, CA, and other byproducts are reported in weight percent.

Table 6
(Not Within the Scope of the Instant Invention)

Sample	Time,hr	%SKA	%CA	%Other
A	0	0	0	0
B	4	7.1	0	4.5
C	24	22.7	0	26.8
D	39	18.3	0	81.7

The second run was carried out with essentially the same procedure with the exception that 0.0015 grams (5.7x10⁻⁶ moles) RhCl₃.3H₂O was used as a catalyst in lieu of the tris(triphenylphosphine)rhodium chloride. The reaction mixture was similarly sampled and analyzed by gas chromatography. These samples are designated as Samples E and F, respectively. The results of the second run are reported, as above, in Table 7:

Table 7

Sample	Time,hr	%SKA	%CA	%Other
E	0	0	0	0
F	4	77.1	0	22.8

The above results demonstrate the preparation of a silyl ketene acetal from another ester of methacrylic acid. These results also demonstrate that RhCl₃.3H₂O is a much more effective catalyst for the preparation of the desired SKA than is tris(triphenylphosphine)rhodium chloride.

Example 5

Three runs were made to prepare a crude silyl ketene acetal from the reaction of (CH₃)₃SiH and an ester of methacrylic acid with the chemical formula,
CH₂ = C(CH₃)COOCH₂CH₂OSi(CH₃)₃ = HEMA.
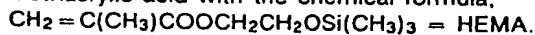
The first two runs used RhCl₃.3H₂O as a catalyst, and the third run used tris(triphenylphosphine)rhodium

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chloride as a catalyst.

1 gram (0.005 moles) HEMA, approximately 0.6 grams (0.008 moles) of $(CH_3)_3SiH$. and 0.004 grams (1.5×10^{-5} moles) of $RhCl_3.3H_2O$ were charged to a sealed, agitated reactor. The reaction was allowed to proceed at ambient temperature, and samples were taken periodically to be analyzed by gas chromatography.
These samples are designated Samples A and B. respectively. The results of these analyses are reported in weight percent (%) unreacted HEMA. desired silyl ketene acetal (SKA).
$(CH_3)_2C = C[OSi(CH_3)_3]$ $[OCH_2CH_2OSi(CH_3)_3]$.
the carbonyl adduct (CA),
$CH_2 = C(CH_3)CH[OSi(OCH_3)_3]$ $[OCH_2CH_2OSi(CH_3)_3]$, and other byproducts. Table 8 is a summary of these analyses as a function of reaction time:

Table 8

Sample	Time,hr	%HEMA	%SKA	%CA	%Other
A	0.5	0	85.5	7.7	6.8
B	1.5	0	84.7	7.4	7.7

The fact that the CA content was still quite high in the above run was attributed to the very short reaction time. A second run was made under similar conditions. 0.5 grams (0.0025 moles) HEMA, approximately 0.5 grams (0.0067 moles) of $(CH_3)_3SiH$, and 0.0044 grams (1.6×10^{-5} moles) of $RhCl_3.3H_2O$ were charged to a sealed, agitated reactor. The reaction was allowed to proceed at ambient temperature, and samples were taken periodically to be analyzed by gas chromatography. These samples are designated Samples C, D, and E, respectively. The results of these analyses are reported below in Table 9.

Table 9

Sample	Time,hr	%HEMA	%SKA	%CA	%Other
C	0.5	16.5	64.5	8.3	10.7
D	1.5	0	73.8	7.8	18.4
E	5	0	64.0	0	36.0

The third run was made similarly to the above runs with the exception that tris(triphenylphosphine)rhodium chloride was used as a catalyst. 1 gram (0.005 moles) HEMA, 0.6 grams (0.008 moles) of $(CH_3)_3SiH$, and 0.015 grams (1.6×10^{-5} moles) of tris(triphenylphosphine)rhodium chloride were charged to a sealed, agitated reactor. The reaction was allowed to proceed at ambient temperature. Again, periodic samples were taken and analyzed. These samples are designated Sample F, G, H, and I, respectively. Table 10 is a summary of these results:

Table 10

(Not Within the Scope of the Instant Invention)

Sample	Time,hr	%HEMA	%SKA	%CA	%Other
F	0.5	100	0	0	0
G	1.5	100	0	0	0
H	4	100	0	0	0
I	24	0	28.0	4.8	67.2

The above results demonstrate the preparation of a silyl ketene acetal from another ester of methacrylic acid. These results further demonstrate that $RhCl_3.3H_2O$ is significantly more effective than tris(triphenylphosphine)rhodium chloride as a catalyst for preparing the desired silyl ketene acetal.

Example 6

81 grams (0.40 moles) of 4-methyl-3.5-dioxyheptyl methacrylate,
$CH_2 = C(CH_3)COOCH_2CH_2OCHCH_3OCH_2CH_3$.

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0.2 grams (7.6×10^{-4} moles) RhCl$_3$.3H$_2$O, and 90 grams of methylene chloride were charged to an agitated reactor. The reactor and its contents were heated to 45°C. The reactor pressure was maintained at 50 psig with nitrogen gas.

A total of 38 grams (0.52 moles) of (CH$_3$)$_3$SiH was added to the reactor at such a rate as to maintain the 45°C. temperature. The reaction mixture was agitated for approximately 10 hours.

· A crude sample was taken and analyzed by gas chromatography. The crude sample was 68 weight percent of the desired silyl ketene acetal (SKA),

(CH$_3$)$_2$C = C[OSi(CH$_3$)$_3$] [OCH$_2$CH$_2$OCHCH$_3$OCH$_2$CH$_3$] .

relative to other byproducts. Negligible amounts of the carbonyl adduct (CA),

CH$_2$ = C(CH$_3$)CH[OSi(CH$_3$)$_3$] [OCH$_2$CH$_2$OCHCH$_3$OCH$_2$CH$_3$] ,

were noted. The major byproduct was the vinyl adduct (VA) .

(CH$_3$)$_3$SiCH$_2$CH(CH$_3$) $\overset{\overset{O}{\parallel}}{C}OCH_2CH_2$OCHCH$_3OCH_2CH_3$.

This example demonstrates the preparation of a silyl ketene acetal from a methacrylic acid ester other than. methyl methacrylate.

Example 7

191 grams of the crude product of the reaction of 4-methyl-3,5-dioxyheptyl methacrylate and (CH$_3$)$_3$SiH, prepared in a manner similar to that described in Example 6, was stripped of low-boilers by conventional means and batch-distilled to recover the desired silyl ketene acetal (SKA). The distillation column used for this separation was estimated to have 15 theoretical trays under the conditions of distillation.

A first distillation run was made to concentrate the desired SKA. During this distillation run, system pressure was maintained at 10-15 mm Hg: pot and overhead temperatures rose to 185° and 125°., respectively; reflux rate was held at 10/1 to 20/1. Three overhead cuts were taken and analyzed by gas chromatography. As noted in Example 6, the crude reaction product has negligible carbonyl adduct (CA), with the vinyl adduct being the major byproduct. The results of this run are listed below in Table 11. Analysis of SKA,VA and unused reactants are reported in weight percent (%).

Table 11

Cut #	Wt,gm	%SKA	%VA	%Reactants
Feed	191	54.7	17.0	12.8
1	30	38.4	2.0	27.9
2	59	86.4	8.2	1.4
3	26	72.7	22.8	0.8

Cut #2 and similar material from a previous distillation were combined in a second distillation run. The same 15-tray column was used. System pressure was 5- 10 mm Hg: pot and overheads temperatures rose to 143° and 94°C., respectively; reflux to the column was held at 2/1. Again, overhead cuts were taken and analyzed by gas chromatography. The results of this run are summarized below in Table 12:

Table 12

Cut #	Wt,gm	%SKA	%VA	%Reactants
Feed	112	80.2	7.6	4.0
1	32	63.5	4.3	15.0
2	41	95.0	1.5	0.6
Pot	21	38.9	37.8	–

This example demonstrates the separation and purification of another silyl ketene acetal material at a purity of 95% or higher.

Example 8

1 gram of methylmethacrylate or MMA (0.01 moles), 0.9 grams (CH$_3$)$_2$(OCH$_3$)SiH (0.01 moles), and 0.002 grams of RhCl$_3$.3H$_2$O (7.3×10^{-5} moles) were charged to a sealed, agitated reactor. The reaction was allowed to take place at ambient temperature. Samples were taken periodically, and these samples were analyzed by gas chromatography. These samples are designated as Samples A, B, and C, respectively.

Table 13 is a summary of crude product analysis as a function of reaction time. Results are reported to point

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out the silyl ketene acetal (SKA),
$(CH_3)_2C = C(OCH_3)$ $[OSi(CH_3)_2(OCH_3)]$.
and carbonyl adduct (CA),
$CH_2 = C(CH_3)CH(OCH_3)$ $[OSi(CH_3)_2(OCH_3)]$.

Table 13

Sample	Time,hr	%MMA	%SKA	%CA	%Other
A	0	100	0	0	0
B	0.3	39.4	49.7	0.4	10.5
C	18	17.7	64.2	0.4	17.7

The above results demonstrate the preparation of a silyl ketene acetal from a partially alkoxylated silane and an ester of methacrylic acid.

Claims

1. A process for the manufacture of silyl ketene acetal material of the general formula selected from the group consisting essentially of
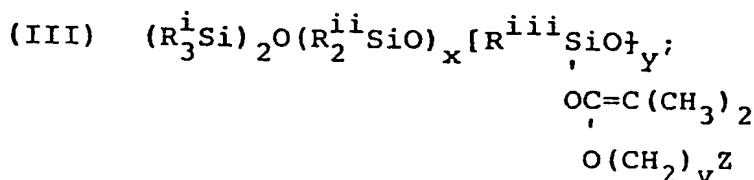
20
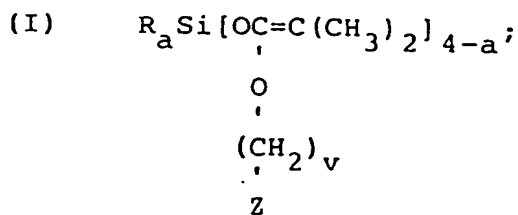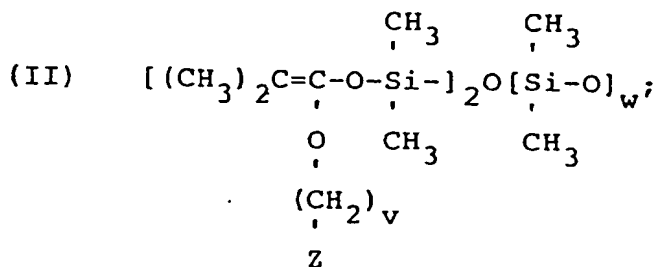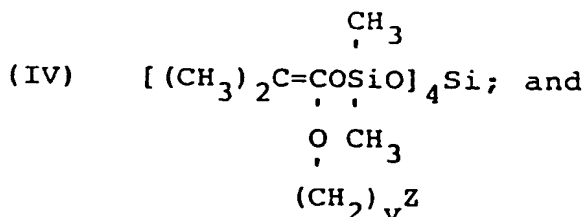
(I) $R_aSi[OC=C(CH_3)_2]_{4-a};$

             O

            $(CH_2)_v$

            Z

(II) $[(CH_3)_2\overset{CH_3}{C}=C-O-\overset{CH_3}{Si}-]_2O[\overset{CH_3}{Si}-O]_w;$

               O CH_3 CH_3

             $(CH_2)_v$

             Z

(III) $(R_3^iSi)_2O(R_2^{ii}SiO)_x[R^{iii}SiO]_y;$

                            $OC=C(CH_3)_2$

                              $O(CH_2)_vZ$

(IV) $[(CH_3)_2\overset{CH_3}{C}=COSiO]_4Si;$ and

             O CH_3

             $(CH_2)_vZ$

wherein R is selected from the group consisting of alkyl radicals containing 1 to 4 carbon atoms, aryl groups, and alkoxy groups containing 1 to 4 carbon atoms;
a has a value of 0, 1, 2, or 3;
v in each case has a value of 0, 1, 2 or 3;
w has a value of 0 to 25;
x has a value of 1 to 100;
y has a value of 1 to 35;

Q is $-OC=C(CH_3)_2;$

        $O(CH_2)_vZ$
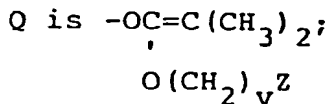
R^i, R^{ii}, and R^{iii} are each independently selected from alkyl groups containing 1 to 4 carbon atoms and aryl groups; Z in each case is independently selected from the group consisting of
(i) -H,
(ii) -OH,
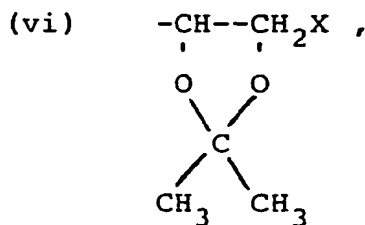(iii) -SiR^{iv}R^{v}R^{vi},
wherein R^{iv}, R^v, and R^{vi} are independently selected from the group consisting of alkyl radicals containing 1 to 4 carbon atoms, aryl groups, and alkoxy groups containing 1 to 4 carbon atoms.
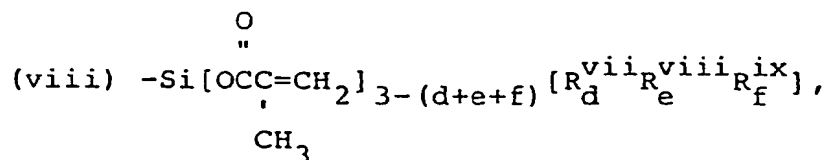(iv) -OSiR^{iv}R^{v}R^{vi},

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(v) -CH(CH$_3$)$_2$,

(vi)

$$-\overset{|}{\underset{O}{C}}H-\overset{|}{\underset{O}{C}}H_2X \;,$$

wherein X is hydrogen or (CH$_2$)$_{0-5}$(CH$_3$).

(vii) -(CH$_2$)$_b$OCH(CH$_3$)O(CH$_2$)$_c$CH$_3$.

wherein b and c each have a value of 1 to 4.

(viii) $-Si[O\overset{O}{\overset{\|}{C}}C=CH_2]_{3-(d+e+f)} \; [R_d^{vii}R_e^{viii}R_f^{ix}]\,,$
      $\qquad\qquad\underset{CH_3}{}$

wherein R^{vii}, R^{viii}, and R^{ix} are independently selected from and have the same definition as R^{iv}, R^v, and R^{vi}; and wherein d, e, and f each have a value of 0 or 1.

(ix) -NR^{x}R^{xi},

wherein R^x and R^{xi} are independently selected from and have the same definition as R^{iv}, R^v, and R^{vi},

(x) -Y,

wherein Y is independently selected from a group consisting of C$_{1-20}$ alkyl, alkenyl, or alkadienyl; C$_{6-20}$ cycloalkyl, aryl, alkaryl, or aralkyl; any of said groups containing one or more ether oxygen atoms within aliphatic segments thereof; and any of such groups containing one or more functional substituents that are unreactive under polymerizing conditions,
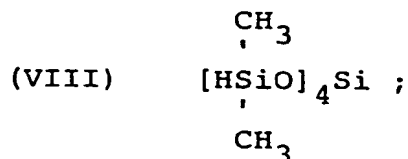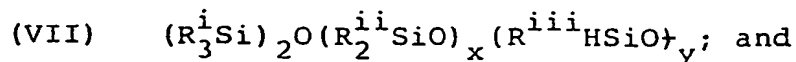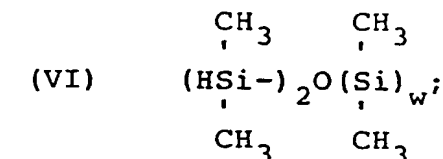
(xi) -N=C=O.

said process comprising (A) contacting a vinylic compound, selected from a group consisting essentially of (i) methacrylic acid and (ii) esters of methacrylic acid having the general formula,

CH$_2$=C(CH$_3$)COO(CH$_2$)$_v$Z,
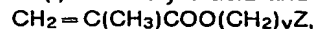
wherein v and Z are as defined above. with hydrogen-containing organosilicon materials having the general formulae.

(V) R$_a$SiH$_{4-a}$;

(VI) $(H\underset{CH_3}{\overset{CH_3}{Si}}-)_2 O (\underset{CH_3}{\overset{CH_3}{Si}})_w;$

(VII) $(R_3^i Si)_2 O (R_2^{ii} SiO)_x (R^{iii} HSiO)_y;$ and

(VIII) $[H\underset{CH_3}{\overset{CH_3}{Si}}O]_4 Si\;;$

wherein. R^i. R^{ii}. R^{iii}. a. w. x. and y have the meanings defined above, in the presence of a rhodium compound containing only inorganic ligands: (B) separating and isolating the desired product from the crude product.

2. The process according to Claim 1. wherein the rhodium compound is RhCl$_3$.3H$_2$O.

3. The process according to Claim 1. wherein the rhodium concentration relative to the vinylic

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compound is at least 50 ppm on a molar basis.

4. The process according to Claim 1, wherein the reaction temperature is in the range of 30° to 80°C.

5. The process according to Claim 1, wherein the reaction of the hydrogen-containing silicon material and the vinylic compound takes place at atmospheric pressure or above.

6. The process according to Claim 1, wherein the hydrogen-containing silicon material and the vinylic compound are reacted over a period of at least one hour.

7. The process according to Claim 1, wherein there is present at least a 12% excess of the hydrogen-containing silicon material relative to the vinylic compound on a molar basis.

8. The process according to Claim 1, wherein distillation is used to separate and isolate the desired silyl ketene acetal.

9. The process according to Claim 1, wherein the vinylic compound is methylmethacrylate, the hydrogen-containing silicon material is $(CH_3)_3SiH$, the rhodium compound is $RhCl_3.3H_2O$ and the rhodium concentration is 50 to 400 ppm on a molar basis relative to the methylmethacrylate, the molar excess of $(CH_3)_3SiH$ relative to methylmethacrylate is greater than 12%, the reaction temperature is 40 to 75°C., the reaction time between methylmethacrylate and $(CH_3)_3SiH$ is at least two hours, the reaction pressure is at least atmospheric pressure, and the silyl ketene acetal,
$(CH_3)_2C=C(OCH_3)$ $[OSiCH_3)_3]$,
is separated and isolated by distillation.

10. The process according to Claim 9, wherein the $RhCl_3.3H_2O$ concentration relative to the methylmethacrylate is 200 to 300 ppm on a molar basis, the molar excess of $(CH_3)_3SiH$ relative to methylmethacrylate is 12 to 25%, the reaction temperature is 45°C to 55°C., the reaction time between methylmethacrylate and $(CH_3)_3SiH$ is 2 to 8 hours, the reaction pressure is essentially at atmospheric pressure, and the silyl ketene acetal content of the final product is greater than 95 weight percent.

11. The process according to Claim 10, wherein the silyl ketene acetal contains less than 1 weight percent of the carbonyl adduct,
$CH_2=C(CH_3)CH(OCH_3)$ $[OSi(CH_3)_3]$.

12. The process according to Claim 10, wherein the reaction pressure is up to 200 psig.

13. The process according to Claim 1, wherein the vinylic compound is 4-methyl-3,5-dioxyheptylmethacrylate, $CH_2=C(CH_3)COOCH_2CH_2OCHCH_3OCH_2CH_3$, the hydrogen-containing silicon material is $(CH_3)_3SiH$, the catalyst is $RhCl_3.3H_2O$ and the catalyst concentration relative to the 4-methyl-3,5-dioxyheptylmethacrylate is 200 to 2000 ppm on a molar basis, the molar excess of $(CH_3)_3SiH$ relative to the 4-methyl-3,5-dioxyheptylmethacrylate is greater than 12%, the reaction temperature is 25° to 55°C., the reaction pressure is at least atmospheric pressure, and the final silyl ketene acetal material,
$(CH_3)_2C=C[OSi(CH_3)_3]$ $[OCH_2CH_2OCH(CH_3)OCH_2CH_3]$.
is separated and isolated by distillation.

14. The process according to Claim 13, wherein the silyl ketene acetal content of the final product is greater than 95 weight percent.

15. The process according to Claim 13, wherein the silyl ketene acetal contains less than 1 weight percent of the carbonyl adduct,
$CH_2=C(CH_3)CH[OSi(CH_3)_3]$ $[OCH_2CH_2OCH(CH_3)OCH_2CH_3]$.

16. The process according to Claim 1, wherein the vinylic compound is
$CH_2=C(CH_3)COOCH_2CH_2OSi(CH_3)_3$,
the hydrogen-containing silicon material is $(CH_3)_3SiH$, the catalyst is $RhCl_3.3H_2O$ and the catalyst concentration relative to the vinylic compound is 300 to 3000 ppm on a molar basis, the molar excess of $(CH_3)_3SiH$ relative to the vinylic compound is greater than 12%, the reaction temperature is 25 to 55°C., the reaction pressure is at least atmospheric pressure, and the final silyl ketene acetal material.
$(CH_3)_2C=C[OSi(CH_3)_3]$ $[OCH_2CH_2OSi(CH_3)_3]$.
is isolated and separated.

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(12) EUROPEAN PATENT APPLICATION

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(54) A process for preparation of silyl ketene acetals.

(57) What is disclosed is a process for the manufacture of increased yields of high-purity silyl ketene acetals, the process comprising a) contacting of methacrylic acid or an ester of methacrylic acid with a hydrogen-containing silicon material in the presence of a rhodium catalyst with inorganic ligands, and b) separation and isolation of the desired product from the crude product.

EP 0 219 322 A3

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,A	JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 111, 1976, pages 43-60, Elsevier Sequoia S.A., Lausanne, CH; I. OJIMA et al.: "Hydrosilylation of alpha,beta-unsaturated nitriles and esters catalyzed by tris(triphenylphosphine)chlororhodium" * Pages 55-57 *	1	C 07 F 7/18 C 07 F 7/04 C 08 G 77/38
P,X	EP-A-0 184 692 (UNION CARBIDE CORP.) * Page 8 *	1-16	

TECHNICAL FIELDS
SEARCHED (Int. Cl.4)

C 07 F 7/00
C 08 G 7/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	05-11-1987	PAUWELS G.R.A.

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